03

(12) UK Patent Application (19) GB (11) 2 218 523 (13) A

(43) Date of A publication 15.11.1989

(21) Application No 8904084.4

(22) Date of filing 22.02.1989

(30) Priority data
(31) 8804717 (32) 29.02.1988 (33) GB

(71) Applicant
United Kingdom Atomic Energy Authority

(Incorporated in the United Kingdom)

11 Charles II Street, London, SW1Y 4QP, United Kingdom

(72) Inventors
Christopher Peter Jones
Patrick Timothy Moseley
David Edward Williams

(74) Agent and/or Address for Service
Clive Stephen Bennett
United Kingdom Atomic Energy Authority, Patents Branch, 11 Charles II Street, London, SW1Y 4QP, United Kingdom

(51) INT CL⁴
G01N 27/12

(52) UK CL (Edition J)
G1N N19B2Q N24S N24X

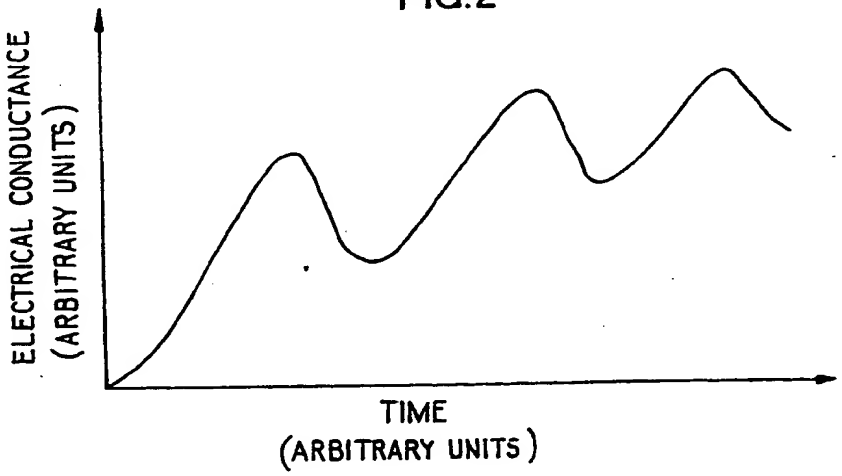
(56) Documents cited
GB 2166549 A GB 2155184 A
Sensors and Actuators, vol 12, Dec 1987 [Netherlands], SR Morrison, "Selectivity in semi-conductor gas sensors", pages 425 to 440 esp 427-8 Sensors and Actuat rs, vol 10, Oct 1986 [Netherlands], SJ Gentry et al, "The role of catalysis in solid-state gas sensors", pages 141-163 esp page 155

(58) Field of search
UK CL (Edition J) G1N
INT CL⁴ G01N 27/12

(54) Sensing the composition of gas

(57) Selectivity in sensing gas composition, using electrical conductance charges in sensing material (e.g. semiconducting oxide) that is catalytic for the decomposition of one or more constituents of the gas, is improved by using either of two alternative methods. In the first, temperature is charged as gas diffuses through a body of the material from a surface of the body to a region in the body where electrical conductance is measured. The resulting conductance/time graph shows respective peaks corresponding to different constituents. In the other method, electrical conductance is measured at two or more different regions (figures 3 and 4) in the material and a composition profile of the gas within the body is obtained as the gas defuses through the body.

FIG.2



GB 2 218 523 A

Gas Sensing

2218523

This invention relates to the sensing of gases using electrically conductive material, e.g. semiconducting oxides, to determine the composition of the gas either qualitatively or quantitatively or both.

Semiconducting oxides are known in the sensing of gases. However, their application is limited by their lack of selectivity. The present invention ameliorates this problem.

In a first aspect, the invention provides a method of sensing the composition of a gas comprising the steps of

(i) contacting a surface of a gas-sensitive, gas permeable, electrically conductive material with the gas, the material being catalytic for the decomposition of one or more constituents of the gas;

(ii) allowing the gas or its decomposition products or both to diffuse through the body of the material from the surface; and

(iii) measuring the electrical conductance of the material either at a region remote from the surface as a function of time as temperature is changed, or at two or more different regions of the material, or both.

In step (iii), the regions may be different in the sense that they are at different distances from the surface in the general direction of said diffusion through the material.

In a first embodiment of the invention, where in step (iii) the conductance is measured as a function of time as

temperature is changed, the gas concentration will be uniform through the body of the material if the temperature is below that it which one or more components in the gas decomposes.

However, if the temperature is the same as or greater than that at which one or more components in the gas decomposes, the gas composition will be different at different distances from the surface within the body of the material because the gas decomposes as it diffuses through the body. Thus, if temperature is changed as a function of time, eg increased linearly or increased sharply from a temperature at which decomposition does not occur to a temperature at which it does occur, the conductance measured will vary with time and show a sharp peak.

The peak arises because the conductance of the material is measured remote from the surface; the response depends on both the temperature and the gas concentration at the region where conductance is measured. Said gas concentration is itself dependent on temperature and the diffusion rate of gas to said region.

If the gas to be sensed contains more than one decomposable gas, the gases will decompose at different temperatures in the above-described embodiment to give more than one peak of conductance measured as a function of time.

If desired, the above peaks may be made sharper by providing the material surface with one or more gas-permeable coatings, which coatings may or may not be catalysts for the decomposition of constituents of the gas. Thus, the coating(s) may either change the diffusion coefficient of the gas only or change the composition gradient in the body of the material by catalysing decomposition of the gas or both.

Furthermore, if desired, the characteristics of the material may be changed by modifying part of its thickness, e.g. its outer part, by incorporating a decomposition catalyst therein.

The heights of and areas under the peaks obtained in the above-described embodiment provide a calculable measure of the concentrations of the constituents of the gas, thereby enabling the present invention to be used as a gas sensor.

In a second embodiment of the invention where, in step (iii), electrical conductance is measured at two or more different regions, a measure of gas composition as a function of position in the material is obtained, the composition, at a particular region, being dependent on diffusion coefficients, reaction rates and temperatures. Since diffusion coefficients and reaction rates are parameters that are specific for specific gases, a method is thereby provided for resolving gases in a gaseous mixture.

One way of measuring conductance at said two or more regions is to provide electrodes at different positions eg in different planes or columns, in the material. Another way is to provide a plurality of electrodes at the same distance from the surface, ie in the same plane, in the material and to measure conductance between pairs of electrodes at different distances apart thereby to measure conductance at said different distances. "In the material" means that the electrodes may be embedded within the material or may be at a surface thereof remote from the surface for contacting the gas.

The above-described second embodiment of the invention may be carried out in conjunction with the above-described first embodiment of the invention to obtain additional

information concerning the composition of the gas. As temperature rises, the gas is consumed by decomposition in the interior of the material and will diffuse from the surface inwardly. The diffusion rate can be modified by providing the surface with a coating of a material such as used in the formation of gas chromatographs, ie gas chromatograph support material. The time dependence of the gas composition profile which can then be sampled will be closely analogous to the output of a gas chromatograph.

The material used in the present invention may be constituted by a single material or by a plurality of constituent materials. In the latter case, each constituent material need not necessarily possess all the above-stated properties of the material to be used, i.e. specific properties may be provided by specific components, for example in the form of a plurality of layers thereof.

"Gas-sensitive" means that the electrical conductance of the material is responsive to variation in the composition of a gas. An example of a material catalytic for decomposition in the invention is a material catalytic for combustion.

A preferred example of material for use in the invention comprises a semi-conducting ceramic such as a semi-conducting oxide which may be a single such oxide or a mixture of such oxides. Examples of such oxides are tin(IV) oxide, zinc oxide, tungsten(VI) oxide, and oxides described in UK Patent Specifications Nos 2 149 120 A, 2 149 121 A, 2 149 122 A, 2 149 123 A, and 2 166 244 A. To render the above oxides catalytic for use in the present invention, they may be provided with a catalyst coating, for example a thin surface covering of finely divided precious metal particles (e.g. of Pt or Pd) or of finely divided particles of another substance, such as another

oxide, that is a decomposition catalyst. A decomposition catalyst may be chosen that is specific for a specific gas. Further, the material to be used may be chosen so that its electrical conductance is sensitive to a decomposition product of a specific gas.

"Gas" in this specification includes vapours and also mixtures not all of the consituents of which are in the gaseous state. The sensing of the gas by the method of the invention may be qualitative or quantitative or both. In order to be sensed, the gas must include at least one constituent to which the material used in the invention is gas-sensitive as defined above. Examples of such constituents are hydrocarbons such as methane, ethane, propane, butane, ethylene, benzene, and toluene; carbon monoxide; hydrogen; ammonia; hydrogen sulphide; nitrogen dioxide; sulphur dioxide; alcohol vapours such as those of methanol, and ethanol; and aldehyde and ketone vapours such as those of formaldehyde, acetone, and methyl ethyl ketone.

The method of the invention may be carried out using a gas sensor comprising the gas-sensitive, gas permeable electrically conductive material mounted on a gas impermeable inert substrate, the sensor optionally being provided with heating means for for heating the material, and the material having a surface for exposure to a gas to be sensed and having means for measuring its electrical conductance at at least one region remote from said surface, preferably at a plurality of regions remote from said surface. Such a sensor is a second aspect of the invention.

The means for measuring conductance may include one or more pairs of electrodes at the same distance from said surface, or more than one pairs of electrodes at different positions remote from said surface.

The gas sensors of the invention may be fabricated by generally known methods of fabrication such as screen printing methods or ceramic tape fabrication processes.

The invention will now be described by way of example as follows. Reference will be made to the accompanying drawings wherein:

Figure 1 is a schematic, sectional diagram of one form of gas sensor of and for use in the invention;

Figure 2 is a graph of electrical conductance against time as obtained using a gas sensor as shown in Figure 1 when the temperature is raised;

Figure 3 is a schematic, sectional diagram of a second form of gas sensor of and for use in the invention; and;

Figure 4 is a schematic, sectional diagram of a third form of gas sensor of and for use in the invention.

In Figures 1, 3 and 4, the same reference numerals will be used for like components.

Referring to Figure 1, a gas permeable layer of a gas-sensitive, semi-conducting ceramic oxide 1 is mounted on a gas impermeable substrate tile 2. The surface of the tile 2 remote from the oxide 1 carries a heater 3. The oxide 1 has an upper surface 4 for contacting the gas to be sensed and carries, embedded therein, a pair of electrodes 5 by means of which the electrical conductance of the oxide 1 can be measured. The oxide 1 is made catalytic for the decomposition of one or more components of a gas to be sensed.

In operation of the sensor shown in Figure 1, the gas to be sensed is caused to impinge upon the surface of the oxide 1. The temperature of the oxide 1 is steadily raised by means of the heater 3 and its electrical conductance at the region where the electrodes 5 are situated measured thereby as a function of time.

The results obtained are shown in Figure 2 for a gas containing three components catalytically combustible at the oxide 1. The graph shows three peaks corresponding to each of the three component gases.

Referring to Figure 3, a gas permeable layer of a semi-conducting oxide 1 as used in the sensor show in Figure 1 is mounted on a gas impermeable substrate tile 2. The oxide 1 has an upper surface 4 for contracting the gas to be sensed and carries, embedded therein, arrays of electrodes 5 for measuring the electrical conductance of the oxide 1. The electrodes 5 are arranged in three sets 6, 7 and 8, each set being at a different distance from the surface 4 of the oxide 1.

In operation of the sensor shown in Figure 3, the gas to be sensed is caused to impinge upon the surface 4 of the oxide 1. The electrical conductance of the oxide 1 is measured between pairs of electrodes 5 in the same set 6, 7 or 8 and/or between pairs of electrodes 5, each of which electrode is in a different set 6, 7 or 8. In this way, a gas composition profile in the oxide 1 is obtained.

Referring to Figure 4, a gas permeable layer of a semi-conducting oxide 1 as used in the sensor shown in Figure 1 is mounted on a gas impermeable substrate tile 2. The oxide 1 has an upper surface 4 for contacting the gas to be sensed and carries, at its interface with the tile 2, a row of parallel electrodes 5 for measuring the electrical conductance of the oxide 1. The electrodes 5 operate in

pairs 9, 10, 11 and 12, whereby the spacing between electrodes is different in each of the pairs 9, 10, 11 and 12.

In operation of the sensor shown in Figure 4, the gas to be sensed is caused to impinge upon the surface 4 of the oxide 1. The electrical conductance of the oxide 1 is measured by means of each of the pairs of electrodes 9, 10, 11 and 12. Each pair 9, 10, 11 or 12 measures the electrical conductance of a different region of the oxide 1: the closer the spacing between the electrodes 5 in a pair 9, 10, 11 or 12, the closer to the electrodes is the region whose conductance is being measured.

This is because, if a pair of electrodes 9, 10, 11 or 12 is closely spaced, the current flow between them "samples" only the part of the body of the oxide 1 which is close thereto since the current path has insufficient distance to spread. On the other hand, if the pair of electrodes 9, 10, 11 or 12 are spaced well apart, the current can spread out and "sample" much more of the body of the oxide 1 as it flows from one electrode 5 to another 5.

Using the sensor shown in Figure 4 enables an electronic map of the composition profile of the gas within the body of the oxide 1 to be generated; the electronic map may be used to resolve the composition of a gaseous mixture and to detect possible poisoning of a sensor.

Claims

1. A method of sensing the composition of a gas comprising the steps of

(i) contacting a surface of a gas-sensitive, gas permeable, electrically conductive material with the gas, the material being catalytic for the decomposition of one or more constituents of the gas;

(ii) allowing the gas or its decomposition products or both to diffuse through the body of the material from the surface; and

(iii) measuring the electrical conductance of the material either at a region remote from the surface as a function of time as temperature is changed, or at two or more different regions of the material, or both.

2. A method as claimed in Claim 1 wherein in step (iii), the regions are different in the sense that they are at different distances from the surface in the general direction of said diffusion through the material.

3. A method as claimed in Claim 1 wherein in step (iii) the conductance is measured as a function of time and temperature is changed from a temperature at which a component in the gas does not decompose to a temperature at which the component of the gas does decompose such that the conductance varies with time to show a peak.

4. A method as claimed in Claim 3 wherein the gas contains more than one decomposable gas, such that more than one peak is shown in the variation of conductance with time.

5. A method as claimed in Claim 3 or Claim 4 wherein the material surface has one or more gas-permeable coatings to enhance the sharpness of the peak or peaks obtained in the variation of conductance with time.

6. A method as claimed in Claim 5 wherein the coating or coatings are such as to change the diffusion coefficient of a gas or gases in the material.

7. A method as claimed in Claim 5 wherein the coating or coatings are such as to change the compositon gradient in the body of the material by catylising decomposition of a gas or gases.

8. A method as claimed in Claim 1 wherein in step (iii) electrical conductance is measured at two or more different regions of the material, and a measure of gas composition as a function of position in the material is obtained, the composition, at a particular region, being dependent on the diffusion coefficient of a gas, reaction rate and temperature.

9. A method as claimed in Claim 8 wherein conductance is measured at the two or more regions by means of electrodes at different positions in the material.

10. A method as claimed in Claim 8 wherein plurality of electrodes is provided at the same distance from the surface in the material and conductance is measured between pairs of electrodes at different distances apart.

11. A method as claimed in any one of the preceding Claims wherein the material is a semi-conducting ceramic.

12. A method as claimed in Claim 11 wherein the semi-conducting ceramic is a semi-conducting oxide or a mixture of semi-conducting oxides.

13. A method as claimed in Claim 12 wherein the or a semi-conducting oxide is tin (IV) oxide, zinc oxide or tungsten (VI) oxide.

14. A method as claimed in any one of the preceding claims wherein the material is provided with a catalyst coating of precious metal or an oxide decompostion catalyst.

15. A method as claimed in any one of the preceding Claims wherein the gas to be sensed includes methane, ethane, propane, butane, ethylene, benzene, toluene, carbon monoxide, sulphur dioxide, methanol vapour, ethanol vapour, formaldehyde vapour, acetone vapour or methyl ethyl ketone vapour.

16. A gas sensor comprising a gas-sensitive, gas permeable, electrically conductive material mounted on a gas impermeable inert substrate, the material having a surface for exposure to a gas to be sensed and means for measuringelectrical conductance of the material at at least one region remote from said surface.

17. A gas sensor as claimed in Claim 16 wherein the sensor has means for measuring electrical conductance of the material at a plurality of regions remote from the said surface.

18. A gas sensor as claimed in Claim 16 or 17 wherein the sensor has heating means for heating the material.

19. A gas sensor as claimed in Claim 16, 17 or 18 wherein the means for measuring conductance includes one or more pairs of electrodes at the same distance from the surface of the material.

20. A gas sensor as claimed in Claim 16, 17 or 18 wherein the means for measuring conductance includes more than one pair of electrodes at different positions remote from the surface of the material.

21. A gas sensor substantially as hereinbefore described with reference to any one of Figures 1, 2, 3 or 4 of the accompanying drawings.

22. A method of sensing the composition of a gas substantially as hereinbefore described with reference to any one of Figures 1, 2, 3 or 4 of the accompanying drawings.

14197 BtH

Published 1989 at The Patent Office. State House. 66 71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office.